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(54) **A laminated packing material with good gas and aroma barrier properties, and a method for the manufacture of the material**

Laminiertes Verpackungsmaterial mit guten Gas- und Aroma-Barriereeigenschaften und Verfahren zu dessen Herstellung

Matériau d'emballage stratifié formant barrière au gaz et à l'arôme et procédé pour sa fabrication

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EP-A- 0 069 642 **EP-A- 0 240 571**
DE-A- 3 212 377

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Description

The present invention relates to a laminated material for packing containers with good gas and aroma barrier properties and/or parts for such containers. The invention also relates to a method for the manufacture of the laminated material.

In packing technology so-called non-returnable or one-way packages have been used for a long time for liquid foodstuffs. A very large group of these packages is manufactured from a laminated material comprising a stiffness layer of paper or cardboard and outer and inner coatings of thermoplastics which on the one hand provide the package with the required liquid-tightness and on the other hand make it possible for the package to be made permanent in its desired geometric outer shape by means of so-called heat-sealing which is based on the surface-fusing of thermoplastic-coated regions of the material folded against one another by means of a supply of heat and pressure so as to form liquid-tight, mechanically strong sealing joints. This material which is often used in packages for less oxygen gas sensitive foodstuffs, e.g. milk, lacks the necessary tightness properties towards gas and certain types of aroma substances and is less suitable, therefore, in packages intended for foodstuffs more sensitive to oxygen gas, e.g. juice, which also contains such readily penetrating and/or readily absorbed aroma substances. To furnish these packages with the required tightness characteristics towards light and the said aroma substances, the material is complemented, therefore, usually by an aluminium foil (Al foil) applied to the inside of the package which provides the package with these necessary gas and aroma barrier properties according to e.g. EP-A-0 069 642.

A serious problem in the case of the packing material described, which comprises an Al foil as a gas and aroma barrier, is that an Al foil because of its low extensibility easily bursts or cracks along particularly exposed regions or so-called crosses during the conversion of the material to packages, and the strains on the material within these regions may even be so strong that the thermoplastic coatings included in the material also rupture and seriously impair the tightness properties of the finished packages as a consequence.

It is also known to provide a packing material with a barrier layer of a polymer material e.g. ethylene-vinyl alcohol copolymer (EVOH), serving as a gas and aroma barrier, but known barrier layers of this type as a rule are moisture-sensitive and lose gas-tightness properties if they are exposed to moisture.

It is an object of the present invention, therefore, to provide guidelines regarding a new laminated material for the manufacture of packing containers with good gas and aroma barrier properties and/or parts for such containers, without, or with negligible, risk of ruptures and crack formation in the material during its conversion to packing containers.

It is a further object to provide a packing material free from moisture-sensitive gas and aroma barrier layers.

It is a further object to provide a laminated material for the manufacture of gas and aroma-tight packing containers with good dimensional stability without the use of a stiffness layer of paper or similar moisture-sensitive material.

The invention is characterized in claim 1 and preferred embodiments are claimed in sub-claims.

According to the present invention the barrier layers use not aluminium or the like metal but an inorganic material in particular silicon compounds like SiO_2 or Si_3N_4 . It is already known to use SiO_2 in combination with Cr according to DE-A-32 12 377 for transparent packaging materials and to use silicon oxide for packaging materials which are used for microwave heating of the good packed within this transparent material according to EP-A-0 240 571. The silicon layers are more than 50 nm thick. However, according to the present invention the thickness of the inorganic barrier layer is between 5 and 50 nm.

It has been found that the inorganic material layers which, for example, may consist of an inorganic silicon compound e.g. silicon dioxide (SiO_2) or silicon nitride (Si_3N_4), in spite of their small material thickness possess extraordinarily good gas and aroma barrier properties at the same time as, thanks to their small material thickness, they are sufficiently flexible and extensible to make possible a conversion of the material to packing container and/or parts for containers without any risk of cracking or bursting even in the most exposed material regions. A further advantage which is obtained by the barrier layer of the preferred type mentioned here is that it is practically completely inert and therefore does not, or only to a negligible degree, affect, or is affected by, the particular contents in the finished package.

It is a further object of the present invention to provide a method for the manufacture of the laminated material.

This object is achieved in accordance with the invention either by the method which is described in the following claim 6 or by the method described in the following claim 7.

The invention will now be described in detail with special reference to the attached drawings, wherein

Figure 1 shows schematically a part of a laminated, weblike material in accordance with the invention,

Figure 2 is a cross-section along the line II-II in Figure 1,

Figure 3 illustrates schematically a method for the manufacture of the laminated material in accordance with the invention, and

Figure 4 illustrates schematically a second method for the manufacture of the laminated material in accordance with the invention.

Figure 1 thus shows schematically a portion corresponding to a whole package length L of a weblike, laminated material 1 in accordance with the invention for the manufacture of packing containers with good gas and aroma barrier properties. As is evident from Figure 2 the material 1 consists of a first partial laminate 1a comprising a carrier layer 2 and a barrier layer 3 of inorganic silicon compounds with tightness properties towards gas and aroma substances applied to the side of the carrier layer facing inwards, and a second partial laminate 1b comprising a carrier layer 4 and a barrier layer 5 of inorganic silicon compounds with similarly good tightness properties towards gas and aroma substances applied to the side of the carrier layer 4 facing inwards. The two partial laminates 1a and 1b are joined to one another by means of an intermediate layer 6 of bonding agent with good adhesion to the mutually facing barrier layers 3 and 5, for example a conventional bonding agent of the surlyn[®], EAA etc. type.

The barrier layers 3 and 5 which may consist, for example, of silicon dioxide (SiO₂) or silicon nitride (Si₃N₄) are applied to their respective carrier layers 2 and 4 by vacuum deposition or by so-called hot stamp technique and have a material thickness of only 5-50 nm (50-500 Å) preferably 20 nm (200 Å).

From the material 1 are manufactured packages with good gas and aroma barrier properties in accordance with conventional technique in that the two longitudinal edge zones 7 and 8 of the material first are combined with one another by means of so-called heat-sealing in an overlap joint so as to form a tube. The tube is filled with the particular contents and is divided into closed packing units by repeated flattening and transverse sealing along zones 9 at right angles to the longitudinal axis of the tube. Thereafter the packing units are separated from one another by means of cuts in the transverse sealing zones 9 and are given the desired final geometric shape, usually a parallelepiped, with the help of a further forming and sealing operation during which the double-walled, triangular corner lugs of the cushionlike packing units are folded in against, and are sealed to, the outside of the packages.

The manufacture of the packages in the known manner described above is facilitated in that the carrier layers 2 and 4 are constituted of thermoplastics, preferably polythene, which thus makes it possible to combine thermoplastic-coated material regions folded towards one another along longitudinal edge zones 7 and 8 and transverse sealing zones 9 respectively by so-called heat-sealing during which the mutually facing thermoplastic coatings with the help of a supply of heat and pressure are made to surface-fuse with one another so as to form liquid-tight, mechanically strong sealing joints. By choosing the carrier layers 2 and 4 of thermoplastic material a further advantage is obtained in that the material 1 is wholly free from, and for its mechanically rigidity and stability is independent of, relatively thick stiffness layers of paper or similar moisture-sensi-

tive material which is often used in conventional packing material. As mentioned earlier, a packing material 1 in accordance with the invention can be manufactured by anyone of the methods illustrated schematically in Figure 3 and Figure 4.

In accordance with Figure 3 the material 1 is manufactured from a first web 10 of prefabricated partial laminate 1a comprising a carrier layer 2 of thermoplastics and a barrier layer 3 of inorganic silicon compounds of 5-50 nm (50-500 Å) thickness applied to one side of the carrier layer by vacuum deposition, and a second web 11 of prefabricated partial laminate 1b comprising a carrier layer 4 and a barrier layer 5 of inorganic silicon compounds of 5-50 nm (50-500 Å) thickness applied to one side of the carrier layer by vacuum deposition. The two webs 10 and 11 (or partial laminates 1a and 1b respectively) are brought together with their respective barrier layers 3 and 5 facing inwards towards one another and are conducted through the nip between a pair of cooperating counterrotating cylinders 12, by means of which the webs are lastingly joined to one another with the help of a bonding agent 6' which at the same time is supplied between the converging webs with the help of an applicator 13 so as to form the finished laminated material 1.

In accordance with Figure 4 the finished laminated material 1 in accordance with the invention is manufactured similarly from a first web 14 (corresponding to partial laminate 1a) comprising a carrier layer 2 and a barrier layer of inorganic silicon compounds of 5-50 nm (50-500 Å) thickness applied to one side of the carrier layer and a second web 15 (corresponding to partial laminate 1b) comprising a carrier layer 4 of thermoplastic material and a barrier layer of inorganic silicon compounds of 5-50 nm (50-500 Å) thickness applied to one side of the carrier layer. The two webs 14 and 15 are conducted via deflection rollers 16 jointly with their respective barrier layers facing towards one another through the nip between a pair of cooperating, counterrotating cylinders 17 with the help of which the webs are lastingly joined to one another by means of a bonding agent 6' which at the same time is supplied between the converging webs with the help of an applicator 18 so as to form the finished material 1. The method according to Figure 4 is distinguished from the earlier method insofar as the manner in which the two partial laminates or webs 14 and 15 are manufactured is concerned and, in particular, the manner in which the respective carrier layers 2 and 4 included in the partial laminates or webs are provided with their respective barrier layers 3 and 5. According to Figure 4 the first web 14 is manufactured so that a web 18 of the thermoplastic carrier layer 2 (as shown on the left in Figure 4) is brought together with a web 19 comprising a polymer carrier 20 (e.g. polyester) which on its side facing towards the web 18 supports a layer 3' of the inorganic silicon compounds of 5-50 nm (50-500 Å) applied by vacuum deposition. The webs 18 and 19 are conducted jointly through the nip between a

pair of cooperating cylinders 21 which according to conventional so-called hot stamp technique transfer and deposit the inorganic layer 3' on the weblike carrier layer 2 to form the first partial laminate or web 14, whilst the polymer carrier 20 freed from the barrier layer 3' is carried away for renewed vacuum deposition and repeated transfer of inorganic material. The other web 15 (corresponding to partial laminate 1b) is manufactured similarly (as shown on the right in Figure 4) in that a web 22 of the carrier layer 4 is brought together with a web 23 comprising a polymer carrier 24 which on its side facing towards the web 22 has a layer 5' of inorganic silicon compounds of 5-50 nm (50-500 Å) deposited by vacuum deposition. the two webs 22 and 23 are conducted jointly through the nip between a pair of heated cooperating cylinders 25 which in accordance with conventional so-called hot stamp technique transfer and deposit the layer 5' on the web 22 so as to form the second partial laminate. The polymer carrier 24 freed from the layer 5' likewise is carried away for renewed vacuum deposition and repeated transfer of inorganic material.

To facilitate the transfer of the respective layer 3' and 5' it may be appropriate, or even necessary, in some case to perform some kind of surface treatment of the webs 18 and 22, e.g. application of a bonding agent of the surlyn®, EAA etc type which also contributes to an increase in adhesion between the layers 3' and 5' and the respective webs 18 and 22.

A laminated material in accordance with the invention can also be used for the manufacture of package parts, e.g. so-called pull-tabs and sealing strips for application to the inside of packing containers, which is particularly desirable in those cases where the package is fabricated mainly from a packing material of conventional type comprising a carrier layer of paper or cardboard which along the longitudinal overlap joint formed during the tube formation has an absorbent cut edge freely exposed towards the inside of the package and which has to be sealed and protected.

Claims

1. A laminated material for packing containers with good gas and aroma barrier properties, comprising

a first partial laminate (1a) comprising a carrier layer (2) and a barrier layer (3) of inorganic material serving as gas and aroma barrier, a second partial laminate (1b) comprising a carrier layer (4) and a barrier layer (5) of inorganic material also serving as gas and aroma barrier, and

an intermediate layer (6) of bonding agent, their respective barrier layers (3, 5) facing one another,

characterized in that

said barrier layers (3, 5) comprise as said inorganic material silicon compounds and have a

thickness of between 5 and 50 nm, each.

2. A laminated material as claimed in claim 1, **characterized in that**

at least one of said barrier layers (3, 5) comprises silicon dioxide (SiO₂).

3. A laminated material as claimed in claim 1 or 2, **characterized in that**

at least one of said barrier layers (3, 5) comprises silicon nitride (Si₃N₄).

4. A laminated material as claimed in one of the preceding claims, **characterized in that**

at least one of said barrier layers (3, 5) comprises a thickness of 20 nm.

5. A laminated material as claimed in one of the preceding claims, **characterized in that**

said carrier layers (2, 4) consist of a thermoplastic material.

6. Method for producing a laminated material as claimed in one of the preceding claims, **characterized in that**

said barrier layers (3, 5) are applied to said carrier layers (2, 4) by vacuum deposition or by hot-stamp technique forming said first partial laminate (1a) and said second partial laminate (1b) wherein the partial laminates (1a, 1b) are joined to one another by an intermediate layer (6) of bonding agent introduced between the barrier layers (3, 5).

7. Method as claimed in claim 6, **characterized in that**

said barrier layer is deposited as a film (3', 5') of said inorganic material on one side of polymer carriers (20, 24) by vacuum deposition whereafter the vacuum-deposited films (3', 5') are transferred from the polymer carriers (20, 24) to said carrier layers (2, 4) by means of hot stamp technique.

Patentansprüche

1. Laminiertes Material für Verpackungsbehälter mit guten Gas- und Aromasperreigenschaften, das folgendes aufweist:

- ein erstes Teillaminat (1a) mit einer Trägerschicht (2) und einer Sperrschicht (3) aus anorganischem Material, die als Gas- und Aromasperre dient,
- ein zweites Teillaminat (1b) mit einer Trägerschicht (4) und einer Sperrschicht (5) aus anorganischem Material, die ebenfalls als Gas- und Aromasperre dient, und einer Zwischenschicht (6) aus einem Bindemittel, wobei ihre jeweiligen Sperrschichten (3, 5) einander zugewandt sind, **dadurch gekennzeichnet, daß** die Sperrschichten (3, 5) als anorganisches Material Siliciumverbindungen aufweisen und jeweils eine Dicke zwischen 5 und 50 nm besitzen.
2. Laminiertes Material nach Anspruch 1, **dadurch gekennzeichnet, daß**
- wenigstens eine der Sperrschichten (3, 5) Siliciumdioxid (SiO_2) aufweist.
3. Laminiertes Material nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß**
- wenigstens eine der Sperrschichten (3, 5) Siliciumnitrid (Si_3N_4) aufweist.
4. Laminiertes Material nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß**
- wenigstens eine der Sperrschichten (3, 5) eine Dicke von 20 nm aufweist.
5. Laminiertes Material nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß**
- die Trägerschichten (2, 4) aus einem Thermoplastmaterial bestehen.
6. Verfahren zur Herstellung eines laminierten Materials nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß**
- die Sperrschichten (3, 5) durch Vakuumabscheidung oder eine Heißprägetechnik auf die Trägerschichten aufgebracht werden, wodurch das erste Teillaminat (1a) und das zweite Teillaminat (1b) gebildet werden, wobei die Teillamine (1a, 1b) durch eine Zwischenschicht (6) aus einem Bindemittel miteinander verbunden werden, das zwischen die Sperrschichten (3, 5) eingebracht wird.
7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet, daß**
- die Sperrschicht durch Vakuumabscheidung als ein Film (3', 5') aus dem anorganischen Material auf eine Seite der Polymerträger (20, 24) abgeschieden wird, woraufhin die im Vakuum abgeschiedenen Filme (3', 5') von den Polymerträgern (20, 24) mittels der Heißprägetechnik auf die Trägerschichten (2, 4) übertragen werden.
- ### Revendications
1. Matériau stratifié pour récipients d'emballage avec de bonnes propriétés de barrière au gaz et à l'arôme, comprenant
- un premier stratifié partiel (1a) comprenant une couche de support (2) et une couche barrière (3) de matériau inorganique servant de barrière au gaz et à l'arôme,
- un second stratifié partiel (1b) comprenant une couche de support (4) et une couche barrière (5) de matériau inorganique servant aussi de barrière au gaz et à l'arôme, et
- une couche intermédiaire (6) d'agent liant, leurs couches barrière respectives (3,5) se faisant face,
- caractérisé en ce que les dites couches barrière (3,5) comprennent comme dit matériau inorganique des composés de silicium et présentent chacune une épaisseur comprise entre 5 et 50 nm.
2. Matériau stratifié selon la revendication 1, caractérisé en ce que
- au moins une des dites couches barrière (3,5) comprend du dioxyde de silicium (SiO_2),
3. Matériau stratifié selon la revendication 1 ou 2, caractérisé en ce que
- au moins une des dites couches barrière (3,5) comprend du nitrure de silicium (Si_3N_4).
4. Matériau stratifié selon l'une quelconque des revendications précédentes, caractérisé en ce que
- l'une ou moins des dites couches barrière (3,5) présente une épaisseur de 20 nm.
5. Matériau stratifié selon l'une des revendications précédentes, caractérisé en ce que

les dites couches de support (2,4) consistent en du matériau thermoplastique.

6. Procédé de production d'un matériau stratifié selon l'une quelconque des revendications précédentes, 5 caractérisé en ce que

les dites couches barrière (3,5) sont appliquées aux dites couches de support (2,4) par dépôt sous vide ou par technique d'estampage à chaud en formant le dit premier stratifié partiel (1a) et le dit second stratifié partiel (1b), dans lequel les stratifiés partiels (1a,1b) sont assemblés l'un à l'autre par une couche intermédiaire (6) d'un agent liant introduit entre les couches barrière (3,5). 10 15

7. Procédé selon la revendication 6, caractérisé en ce que

la dite couche barrière est déposée sous la forme d'un film (3',5') du dit matériau inorganique sur une face de supports polymères (20,24) par dépôt sous vide, après quoi les films déposés sous vide (3',5') sont transférés des supports polymères (20,24) aux dites couches de support (2,4) au moyen de la technique d'estampage à chaud. 20 25

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Fig. 1

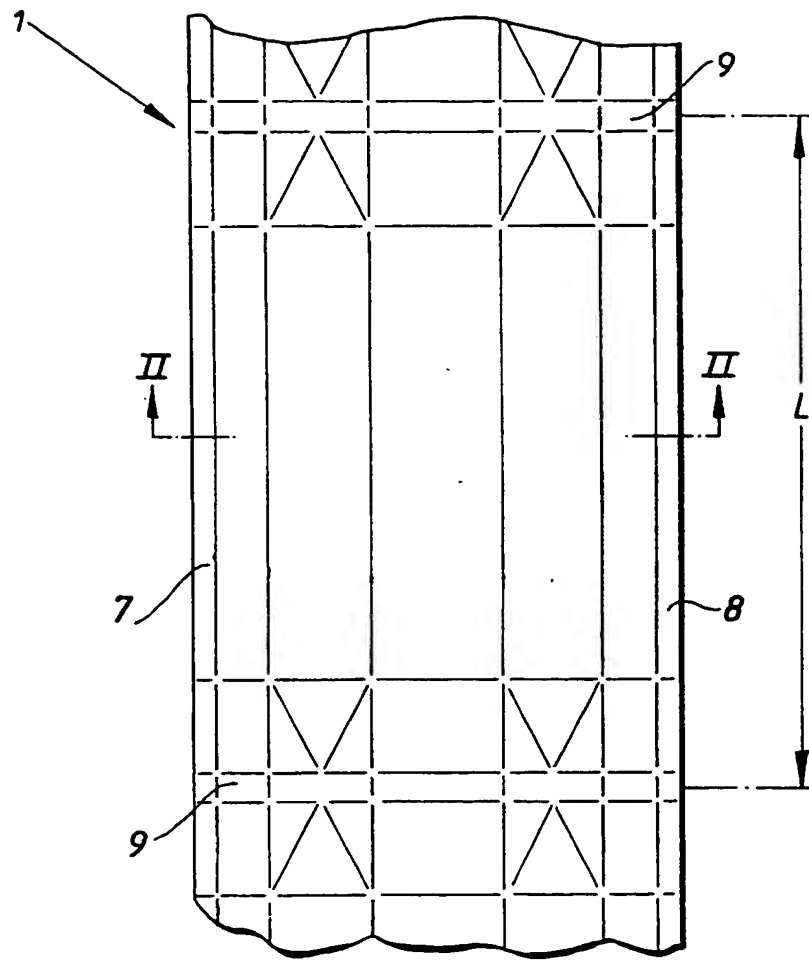


Fig. 2

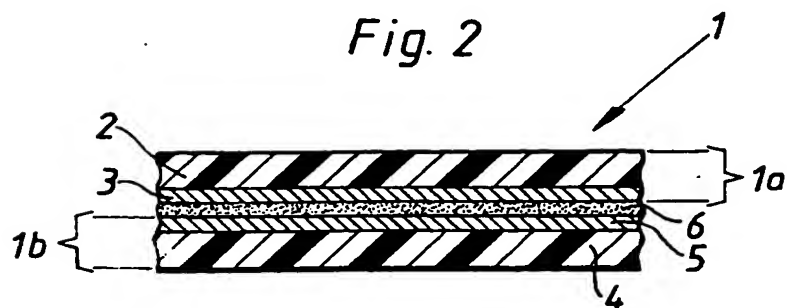


Fig. 3

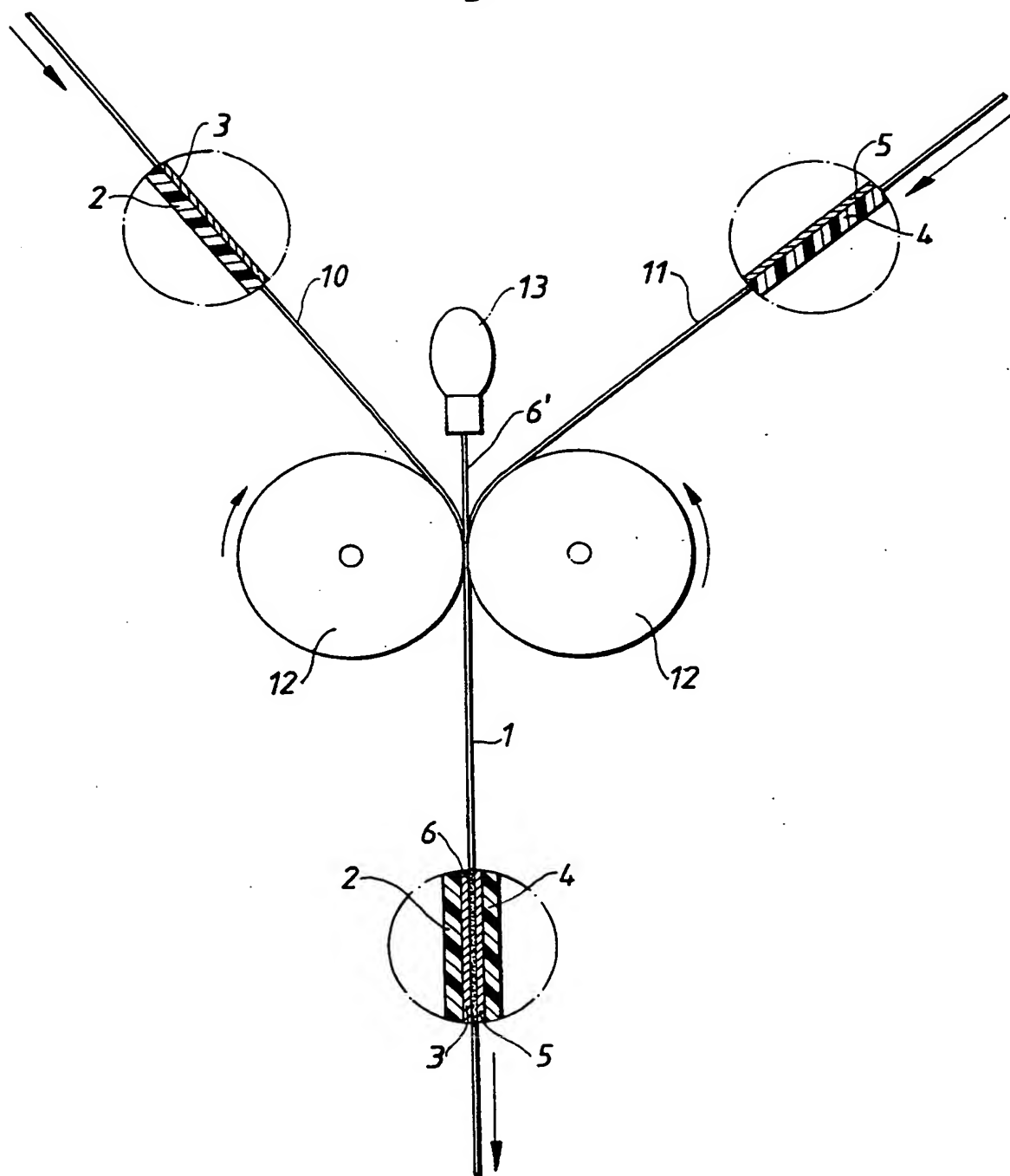


Fig. 4

